

Reactively compatibilized polymer blends: Interfacial chemical reactions during melt-extrusion

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Abstract: Reactive compatibilization of immiscible polymer blends is a method which is very often used to obtain well dispersed and stabilized phase morphologies (ref. 1,2). The technique of reactive compatibilization is based on the in-situ formation of a block- or graft copolymer at the interface between the phases of a polymer blend during melt-mixing. In some cases, a third polymer, which is miscible with one of the blend components and reactive with the other, can be used for the formation of a compatibilizing copolymer at the interface (ref. 1,2). This strategy is applied here : SMA2 is miscible with PS (and PPO) and its anhydride groups can react with the amino end groups of PA-6 giving rise to the formation of a graft copolymer at the interface. In this paper, a comparison will be made between the reactively compatibilized blend systems PA-6/(PS/SMA2) and PA-6/(PPO/SMA2). The interfacial reaction was analyzed in the extruded blends PA-6/(PS/SMA2) and PA-6/(PPO/SMA2). An extraction procedure was developed to remove the PA-6 phase from these extruded blends and to characterize the remaining phase PS/SMA2 (or PPO/SMA2) with FTIR. In this way, the amount of reacted MA-groups can be determined.

EXPERIMENTAL

Materials

The characteristics of the blend components considered are given in Table 1. Two different molecular weights of semicrystalline polyamide 6 were used. PPO is an amorphous polymer with a T_g of ± 218 °C. PS and SMA2 are both amorphous polymers with a T_g of 100 and 104 °C respectively. The number after SMA denotes the weight % maleic anhydride in SMA.

TABLE 1 The molecular characteristics of the different blend components

Material	Mw	Method
PA-6	18 000	[η] in HCOOH/H ₂ O 85/15 at 25°C
PA-6	24 000	
PPO	54 000	GPC in CHCl ₃
PS	180000	GPC in THF
SMA2	145000	

Blend Preparation and Morphological Characterization

Different compositions of the blends were prepared in a conical twin screw mini-extruder designed by DSM-Research (The Netherlands). The mixing chamber was saturated with nitrogen gas during blending to avoid oxidative degradation of the blend components. The mixing temperature was kept constant at 240°C for the blend system PA-6/(PS/SMA2) and 270 °C for the blend system PA-6/(PPO/SMA2); the screw speed was 100 rpm.

Miscible preblends (PS/SMA2) (and PPO/SMA2) were prepared in the mini-extruder. These preblends were cut into small pieces, and subsequently used in the final extrusion step. In this final extrusion step, the PS/SMA2 (or PPO/SMA2) preblend is firstly fed into the mini-extruder, immediately followed by PA-6.

The blending time is recorded from the moment all the PA-6 is added. This extrusion procedure in two steps is chosen to be sure that all the SMA2 is mixed well with the PS (or PPO) phase. After blending, the extruded polymer strand was quenched in a mixture of isopropanol/CO₂ in order to freeze in the phase morphology. In all blends studied, PA-6 forms the matrix while the dispersed phase consists of the miscible components PS/SMA2 (or PPO/SMA2).

The extruded polymer blend strand was kept in liquid nitrogen for some time and a brittle fracture was performed. This brittle surface was etched with chloroform (a good solvent for PPO, PS and SMA2) for 48 hours at room temperature in order to dissolve the dispersed phase PS/SMA2 or PPO/SMA2. The etched surface was kept under vacuum before coating it with a gold layer of ± 40 nm. After gold coating, the blend morphology was examined with a Phillips XL20 scanning electron microscope.

Characterisation of the Interfacial Reaction

A procedure was developed to remove the PA-6 matrix phase from the blends and to quantify the amount of non-reacted maleic anhydride groups by means of FTIR. Firstly, the blends are put in 100 mL solution of HCl, 6N at 85 °C for 40 hours. This leads to the hydrolysis of the PA-6 matrix and the resulting PA-6 monomers are soluble in HCl, 6N (ref. 3,4). It was shown in the literature (ref. 5,6) that the imide links are stable under these conditions and will not undergo hydrolysis. The dispersed PS/SMA2 (or PPO/SMA2) particles coagulate together and form a solid precipitated phase. This phase is filtered and washed with water several times to remove all PA-6 monomers. Then, the PS/SMA2 phase is heated at 200°C (240 °C for PPO/SMA2) for 45 minutes in order to close the eventually hydrolyzed anhydride groups; this proved to be an effective procedure to convert a diacid back into its anhydride.

Finally, the PS/SMA2 (or PPO/SMA2) phase is again dissolved in CHCl₃, and a droplet of this solution is put on a KBr disk. CHCl₃ is evaporated at room temperature and the thin film thus obtained is analyzed by FTIR. The absorption of the anhydride group (1780 cm⁻¹) is very suitable for quantification. In the case of PS/SMA2, the two styrene peaks at 1453 cm⁻¹ and 1492 cm⁻¹ are chosen as reference peaks. A baseline is drawn on the FTIR-spectrum and the height of the maleic anhydride (MA) peak is divided by the area of the two styrene (S) peaks. Such a spectrum is shown in Fig. 1 for PS/SMA2 together with the expected structure of SMA after reactive blending with PA-6 followed by the extraction procedure. In the case of PPO/SMA2, the height of the maleic anhydride (MA) peak is divided by half the area of the PPO peak at 857 cm⁻¹. The peak absorbance ratio can only be related to a real concentration of MA by means of a calibration curve. For this reason, different mixtures PS/SMA2 (and PPO/SMA2) were dissolved in chloroform. These mixtures have a known MA-concentration. For each calibration mixture, the peak absorbance ratio was measured by means of FTIR; all data were fitted and in this way the MA-content of samples can be determined by FTIR.

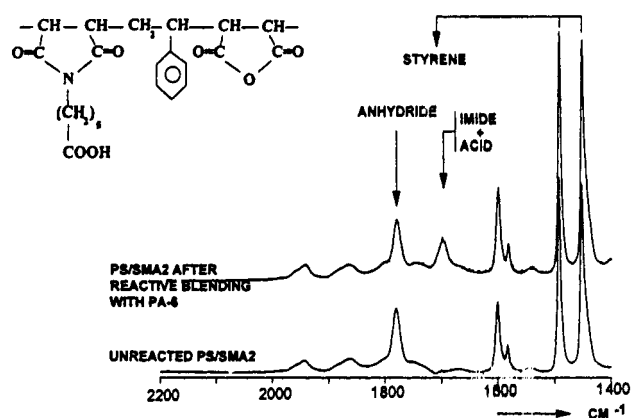


Figure 1 FTIR spectrum of PS/SMA2 before and after reactive blending with PA-6 together with the expected structure of SMA

RESULTS AND DISCUSSION

Blends PA-6/(PS/SMA2)

The concentration of SMA2 in the blend PA-6/(PS/SMA2) was varied. Different compositions were prepared; all blends have 80% PA-6 as a matrix and 20% dispersed PS/SMA2 particles with varying PS/SMA2 weight ratios. Two different molecular weights of PA-6 were used ($M_w = 44\ 000$ and $M_w = 18\ 000$). Firstly, the phase morphology of these blends is discussed. For the uncompatibilized blends PA-6/PS, the dispersed PS-particles are larger in the low molecular weight PA-6 matrix. This can easily be explained on the basis of the lower dispersive forces and the higher coalescence rate in a low molecular weight matrix. However, this trend is inverted in the blend PA-6/(PS/SMA2) 80/(16/4); the dispersed particles are much larger in the higher molecular weight PA-6 matrix. However, at a higher magnification, a second population of very small particles is observed in the case of the high molecular weight PA-6 matrix (Fig. 2).

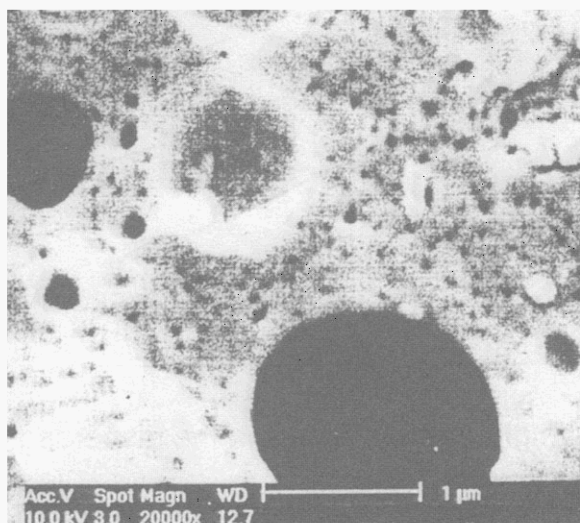


Figure 2 SEM micrograph of the PA-6/(PS/SMA2) blend with a composition 80/(16/4) (M_w PA-6 = 44 000)

This behaviour is interpreted in the following way :

- i) It is very likely that, in the case of the high molecular weight PA-6, the graft copolymer has left the interface resulting in a bimodal particle size distribution as seen in Fig. 2. In a previous paper (ref. 7), it was concluded that, in the blend system PA-6/(PMMA/SMA), the graft copolymer is removed from the interface due to the weak miscibility of the SMA main chain of the graft copolymer with the dispersed phase and the large forces exerted on the PA-6 side chains segments of the graft copolymer in the extruder.
- ii) For the blend system PA-6/(PS/SMA2), the miscibility of PS and SMA2 can also be considered as relatively weak (ref. 8).
- iii) In the case of the low molecular weight PA-6, a bimodal distribution is not observed. Very probably, the graft copolymer has not left the interface in this case, which is also indicated by the much better compatibilizing effect compared to the high molecular weight matrix. It is not completely clear why the graft copolymer is only repelled from the interface in the case of the high molecular weight matrix but we assume that the higher viscosity and the higher shear forces in a high molecular weight matrix enhance this phenomenon.

The percentage reacted MA-groups for the blends PA-6/(PS/SMA2) is given in Fig. 3 as a function of the SMA2-content. The percentage reacted MA-groups decreases with increasing SMA2-content. The observed trend in Fig. 3 can easily be explained. When the concentration of SMA2 is increased, the

interface will become saturated with SMA2, and as a consequence, some SMA2-molecules will not be able to reach the interface and to react. This will of course decrease the percentage of reacted MA-groups. The blend PA-6/PS/SMA2 80/(16/4) with the high molecular weight PA-6 (bimodal distribution) has a very high conversion level of MA. It should be noted that once the graft copolymer has left the interface, the steric hindrance will be lower at the interface and the other unreacted SMA2 chains can also diffuse from the core of a dispersed particle towards the interface.

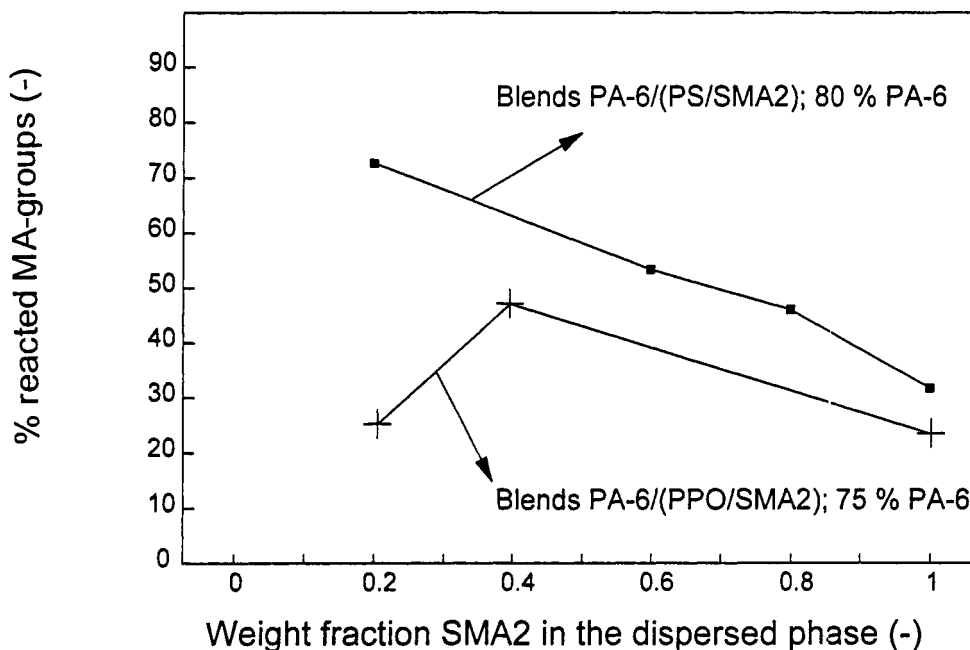


Figure 3 The percentage reacted MA-groups as a function of the SMA2 content in the dispersed phase. Mw PA-6 = 44000

Blends PA-6/(PPO/SMA2)

Blends PA-6/(PPO/SMA2) (Mw PA-6 = 44 000) were extruded during 15 minutes; these blends contain 75 % PA-6 and 25% PPO/SMA2 in a varying ratio. Concerning the FTIR-results after extraction of PA-6, it was found that the % reacted MA-groups reaches its highest value for an intermediate SMA2-content (fig.3). At low SMA2-content (PPO/SMA2 20/5), the reaction extent is limited due to the limited amount of interfacial area and the absence of diffusion on account of the higher viscosity of PPO (only 26 % reacted MA-groups). At intermediate SMA2-content (PPO/SMA2 15/10), the % reacted MA-groups has increased to 46 %. There are two important factors which can explain this increase. Firstly, the amount of interfacial area is increased and a higher percentage of SMA2 will be close enough to the interface to react with PA-6. It can be stated that the interfacial reaction accelerates itself; the interfacial reaction leads to a higher amount of interfacial area and in this way more SMA2 molecules are close enough to the interface to undergo the interfacial reaction. Secondly, the viscosity of the phase PPO/SMA2 will be decreased by increasing the SMA2 content which will favour the diffusion of the SMA2 towards the interface. Finally, at high SMA2-content (PPO/SMA2 0/25), the % reacted MA-groups is again lower (25%). In this case the reaction extent is limited because part of the SMA2-chains will be located in the core of the dispersed particles without participating in the interfacial reaction.

This result is in complete contrast with that of the previous paragraph where the % reacted groups was measured for the PA-6/(PS/SMA2) blends. In this blend system, the diffusion of SMA2 is fast enough to reach the interface within the applied extrusion time. In such a system, an increase of the SMA2-content does not accelerate the interfacial reaction and a continuous decrease of the % reacted MA-groups as a function of the SMA2-content is found.

All the blends PA-6/(PPO/SMA2) were also prepared with a low molecular weight PA-6 matrix ($M_w = 18\ 000$) during 15 minutes of extrusion. For the non compatibilized blends, the dispersed particle size is very large. This lower molecular weight PA-6 matrix has a lower viscosity and its dispersive force is too low to generate a fine dispersion. According to our concept of limited diffusion which was presented here above, the amount of SMA2 which will be close enough to the interface to react with PA-6 will be very low. This was confirmed by the analysis of the % reacted MA-groups in the blend with a composition 75/(20/5) : the 'peak ratio MA/PPO' after extrusion was still unchanged compared to the original value.

In the blend with a composition 75/(15/10), the percentage reacted MA-groups is increased ($\pm 10\%$) compared to the blend with a composition 75/(20/5). This increase is very analogue to the blends with the higher molecular weight PA-6, but the reaction extent is much lower due to the limited amount of interfacial area. These data give an extra confirmation that the graft copolymer formation is limited to the SMA2 chains which are close enough to the interface.

CONCLUSION

The % reacted MA-groups in the blend system PA-6/(PPO/SMA2) reaches a maximum as a function of the SMA2-content due to the limited diffusion and the increase in interfacial area via reactive compatibilization. The interfacial reaction accelerates itself. In the blend system PA-6/(PS/SMA2), the % reacted MA-groups decreases as a function of the SMA2-content. The diffusion of SMA2 towards the interface is fast enough in this system and an increase of the SMA2-content will not accelerate the interfacial reaction but saturation of the interface will occur. However, in this blend system, the location of the graft copolymer at the interface is not stable and it loses its compatibilizing effect. This phenomenon is only observed for the higher M_w PA-6; it is probably caused by the limited miscibility between PS and SMA2.

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